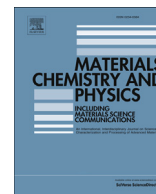




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Evolution of iron nanoparticles by controlling oxidation states for carbon nanotubes growth

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HIGHLIGHTS

- Effect of the electrical conductivity of substrate on CVD growth by thermal CVD was discussed.
- Oxidation states of Fe film as a catalyst were modulated by the electrical conductivity of substrate.
- Controlled catalytic nanoparticles were obtained on the substrate after annealing for CNT growth.
- The electrical conductivity of substrate could be as one of CNTs growth parameter by thermal CVD.

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ABSTRACT

One of the keys to understanding the growth mechanism of carbon nanotubes (CNTs) is the influence of the oxidation states of the iron catalyst nanoparticles. We examined the effect of the oxidation states of iron nanoparticles, which could be controlled by varying the electrical conductivity of the silicon substrate, on the growth of CNTs during thermal chemical vapour deposition. Since the thermal conductivities of the silicon substrate is proportional to its electrical conductivities, thereby catalytic iron thin film on the silicon substrate with higher thermal conductivity could be more affected at the same temperature. The *p*-type silicon substrates with the electrical conductivities of $1.7 \times 10^{-3}/\Omega$ cm (substrate U) and $2.8 \times 10^2/\Omega$ cm (substrate H), respectively, were used in this work. The substrate H allowed that the oxidized iron was more reduced to metallic iron and iron particles grew increasingly larger during annealing under NH_3/Ar environment at 900 °C. This size increase is due to the tendency of the reduced metallic iron particles to agglomerate on the substrate. By showing that the oxidation states of iron catalyst could be controlled by the electrical conductivities of the silicon substrates, resulting in the evolution of catalytic nanoparticles for CNTs growth, the electrical conductivities of the substrate could be used as a key parameter for understanding CNTs growth mechanism.

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1. Introduction

Carbon nanotubes (CNTs) have attracted much attention due to their outstanding properties. Especially, the electrochemical performance of carbon nanotubes (CNTs) has been widely studied in the field of electrochemical sensors [1–3], catalytic electrodes [4], and energy storage/supply [5–7] applications because of their beneficial properties, such as large surface areas, excellent electrochemical properties, high electron-transfer rates, and minimum

surface fouling effects.

A consensus on the importance of controlling the morphology and structure of CNTs has been established [8–13]. Various parameters such as the thickness of catalytic metal films [14], annealing temperature [15], supporting layers [16], types of substrate [17], and ammonia gas flow rate [12,18] have been utilized for controlling the formation of catalytic metal particles on the surface of the substrate in the process of thermal chemical vapour deposition (CVD).

For understanding the growth mechanism of CNTs, one of the important questions is as to what the state and behaviour of the catalysts are during the synthesis. Modelling on the nucleation of metal catalyst particles by heat treatment has been studied using

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thermodynamics and statistical theories [19–22]. It was found that the resultant particles after heat treatment exist as oxidized metal state rather than pure metal state [23]. The roles of oxygen or oxidative species in the metal-on-oxide system have been experimentally demonstrated for the evolution of metal particles. Oxygen always exists in the reaction chamber in a small amount, whether from trapped air or elsewhere. In an early study, Baker et al. [24] reported on the catalytic activity of the iron subgroups of Fe, FeO, and Fe₂O₃ in the formation of carbon filaments. Oxide substrate plays an important role in the catalytic activity. The morphology and orientation of the metal particles on the oxide surface could be modified by the oxidation/reduction treatment of the substrate and overlayer [25]. Oxygen etches carbon shell open and alters the carbon precipitation process in metals, resulting in the growth of single-walled CNTs [26]. Furthermore, Okida et al. [27] reported that there existed the correlation between CNT growth and the oxidation state of catalysts.

When the metal thin film is annealed, particles are formed by film coarsening. And then, they agglomerate through surface migration, driven by a thermally activated process resulting in a minimization of the surface energy of the film-substrate combination. The agglomeration process of metal particles has been considered under the metal-on-oxide system. Gadkari et al. [28] investigated the agglomeration behaviour of some metal films on the surface of SiO₂ as a function of annealing temperature. They found that the presence of SiO₂ layer reduced the tendency of the film to agglomerate. In addition, aggressive gases, such as NH₃ or H₂, which can reduce oxidized metal particles, are effective for the surface reconstruction [12]. If the iron strongly interacts with an oxygen-containing substrate, such as Al₂O₃ layer, or it is oxidized itself, the mobility of iron atoms is precluded on the surface [16]. Namely, reduced metallic iron particles possess more mobility and agglomerate to form bigger particles.

Although the strong relationship between the oxidation and reduction reaction of the catalyst and the formation process of the metal particles has been systematically investigated [29–32], a detailed understanding of controlling the chemical states of catalysts in order to grow the desired form of CNTs still needs to be done. Recently, we suggested that the electrical conductivity of silicon substrate, which has not been considered thus far, could be used as a control parameter for the growth of CNTs by thermal CVD without altering other growth parameters [33]. We found that the average size of the catalytic Fe particles clearly increased as the electrical conductivity of the Si(100) substrate increased, resulting in the synthesis of the CNTs with large diameters. The iron particles promoted agglomeration on the Si(100) substrate with a higher electrical conductivity. Our question is how the electrical conductivity of Si(100) substrate affects both the agglomeration of iron particles and the growth of CNTs by CVD. Moreover, another question is that whether there is a correlation between the oxidation states of catalytic iron metal particle and electrical conductivity of Si(100) substrate. Lastly, is it possible that the oxidation states of catalytic iron metal particle are affected and even modified by the electrical conductivity of silicon substrate? We believe that the electrical conductivity of substrate opens up another key issue to understand and control the formation of catalytic particles for CNTs growth.

In this paper, we have investigated in detail the effects of the electrical conductivity of silicon (100) substrates on both the structure and morphology of iron particles and growth of CNTs using thermal CVD. We analysed the oxidation states of the Fe catalysts using X-ray photoelectron spectroscopy (XPS) and Cs-corrected energy filtered transmission electron microscopy (EF-TEM) for measurements of electron energy loss spectroscopy (EELS). Changes in morphology of iron film on Si(100) substrates

with different electrical conductivities were systematically investigated by using field emission-scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). The correlation between the oxidation states of the catalysts and the formation of catalytic particles is evaluated and discussed. Based on those results, we ensure that the oxidation states of catalytic iron particles could be controlled and contributed to the formation of graphite layers for the CNTs growth.

2. Experimental

2.1. Formation of Fe nanoparticles

P-type Si (100) substrates with electrical conductivities of $1.7 \times 10^{-3}/\Omega$ cm (substrate U) and $2.8 \times 10^2/\Omega$ cm (substrate H) were prepared. The electrical characteristics for Si substrates of U and H are summarized in Table 1, which were measured by Hall measurement equipment (Ecopia, HMS-3000). Silicon oxide layers on the substrate surfaces were removed by using a conventional process with a buffer oxide etching solution. A 24-nm-thick Fe film was directly deposited onto the silicon substrate by using a thermal evaporator. The Fe film-deposited silicon substrates were then loaded into a thermal CVD reactor without any pretreatment. The CVD chamber was on standby and pumped down to a low pressure of less than 20 mTorr. Argon (Ar) gas was flowed into the chamber at a rate of 1000 standard cubic centimeters per minute (sccm). At the same time, while ammonia (NH₃) gas with a flow rate of 140 sccm was flowed into the reactor, the substrates were heated for 30 min to the growth temperature of 900 °C at 60 Torr, and then maintained at 900 °C for 5 min at around 760 Torr.

2.2. Growth of carbon nanotubes

Carbon gaseous source, especially acetylene (C₂H₂) gas in this work, was supplied at a flow rate of 20 sccm for 5 s at 900 °C and around 760 Torr to synthesize the CNTs. After CNT growth, the chamber was cooled down to room temperature and pumped down to a low pressure of less than 20 mTorr. Again, the same growth parameters were used for all samples, with the exception of the electrical conductivity of the Si substrate.

2.3. Characterization

This work has focused on the formation of catalyst particles and their oxidation status by annealing. However, the samples must be taken to the instrument for ex-situ analysis. Therefore, we have endeavored that the exposure of samples to air and moisture was minimized. Once the samples were taken out from the chamber cooled off to room temperature, each sample was divided into small pieces for the characterization by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4300SE), atomic force microscopy (AFM, PSIA, XE-100), Cs-corrected energy filtered transmission electron microscopy (EF-TEM, JEOL, JEM-2200FS), and X-ray photoelectron spectroscopy (XPS, Kratos. Inc, AXIS-NOVA), respectively. And then the samples were immediately placed into a vacuum seal bag and sealed until the measurement. Surface roughness of annealed catalytic film was characterized in a non-contact mode of AFM. The seven images were acquired in a region of $1 \times 1 \mu\text{m}^2$ per each sample, thus providing the averaged surface roughness values. For TEM observation of Fe particles on the substrate, the substrates were mechanically thinned, dimpled by dimple grinder and polished by precision ion polishing system operated at Ar⁺ acceleration voltage of 3–5 keV. Electron energy loss spectroscopy (EELS) spectra were includes the following core edges: Fe, L₂₃–edge at 708eV; O, K-edge at 532eV; Si L-edge at

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